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(54) Title: ELASTIC ARTICLES AND USES THEREOF

(57) Abstract: The present invention relates to elastic articles comprising a polymeric matrix and an active ingredient, such as detergent ingredients, typically to be delivered to aqueous environment. Highly preferred active ingredients include enzymes. A preferred elastic article is a foam which is stable upon contact with air but dissolves, disintegrates or disperses in water. The invention also relates to compositions containing the articles and methods for making the articles.

WO 01/25323 A1

## ELASTIC ARTICLES AND USES THEREOF

### Technical Field

The present invention relates to elastic articles, typically beads, particles or tablets,  
5 comprising a matrix of a polymeric material, a plasticiser and/ or water and an active  
ingredient, such as detergent ingredients, typically to be delivered to an aqueous  
environment. The invention also relates to compositions containing the elastic articles  
and methods for making the elastic articles.

### Background to the Invention

Compositions such as cleaning products and personal-care products, cosmetics and  
pharmaceuticals, often comprise active ingredients which are to be delivered to water or  
which are required to be active in aqueous conditions, but, which are sensitive to moisture,  
temperature changes, light and/or air during storage. Also, these compositions often  
15 contain ingredients which may react with one another. Therefore, such ingredient or  
actives are often protected or separated from one another by coating agents or  
encapsulating agents. For example enzymes, used in detergents, are often incompatible  
with alkaline or acid materials, bleaches, moisture and light and thus coated to protect  
them. Because the active materials generally need to be delivered in aqueous conditions,  
20 the coating materials need to be chosen such that the coating and actives dissolve or  
disperse well in water.

Another problem with many solid ingredients, in particular enzymes, is that they tend to  
form dust during handling due to physical forces. This not only creates waste product,  
25 but the dust can also cause hygiene and health problems. Again, coating of the ingredients  
can improve this problem to some extent. The problem with many coated particles is that  
they do not always exhibit sufficient impact resistance during handling. Thus, even when  
handling encapsulated enzyme particles, dust is formed which causes health and hygiene  
problems. One proposed solution to reduce dust formation is to make these granules  
30 harder.

The inventors have now found an improved method of protecting actives and delivering actives to liquid environments such as aqueous environments. They found that specific elastic articles having a matrix, for example a core or coating, made from polymeric material having a specific glass transition temperature, are very impact robust and the active ingredient incorporated in such an article are effectively protected, not only against air-moisture and chemical reactions but also against physical forces. Thus, the resulting elastic articles have been found to be very impact resistant, thus resulting in reduced braking-up or abrasion during handling and reduced dust formation. For example, elastic particles or beads with enzymes can thus be obtained which are safer and more efficient to handle. Moreover, these articles can be made such that they still deliver the actives very efficiently to liquid, e.g. aqueous, environments. Preferably the article is in the form of a foam article, which is air-stable under normal humidity storage conditions, but unstable upon contact with water, to thus deliver the actives.

The elastic article is useful in any product, in particular useful in cleaning products, pharmaceutical products, personal-care products, cosmetic products and fabric-care products.

#### Summary of the Invention

The invention relates to an elastic article comprising

- a) an active ingredient;
- b) a matrix formed from a polymeric material and a plasticiser, provided that when the plasticiser consist of water, the level of water is at least 3% by weight of the article (based on free-moisture level),

whereby the article is capable of delivering the active to a liquid environment, and whereby the matrix has a glass transition temperature (T<sub>g</sub>) below 50°C, preferably below 40°C, and whereby the active ingredient may be present in the matrix, or may be outside the matrix.

Preferably the matrix has a Tg of less than 20°C or even from -20°C or even -10°C to 10°C or even to 0°C, and preferably the matrix has such an elasticity that it has an elastic modulus of less than 1GN.m<sup>-2</sup>, preferably less than 0.5 or even 0.1GNm<sup>-2</sup>.

- 5 It may thus be preferred that the active ingredient is present in the matrix, for example that the polymer material and active ingredient are homogeneously mixed within the matrix, or for example, it may be preferred that the matrix is in the form of a coating or layer around the active ingredient.
- 10 The elastic article preferably releases the active ingredient or part thereof upon contact with water, the article and the matrix preferably partially or completely disintegrating, dispersing, denaturing and/ or dissolving upon contact with water.

The elastic article is preferable an elastic foam article. The elastic article may preferably  
15 be in the form of particles or beads.

Preferably the active ingredients are cleaning actives, personal-care or cosmetic actives or pharmaceutical actives. The elastic article may also contain mixtures of active ingredients, which may be particularly useful to improve the storing of active ingredients  
20 which can react with one another. By use of the elastic article, it can be achieved that such ingredients only become active once released into the aqueous conditions. The article may comprise full compositions, or only some or one active ingredients to be incorporated in such compositions.

25 The invention also relates to processes for making the elastic article, and compositions comprising the elastic article.

The invention also relates to the use of elastic articles according to the invention to deliver active ingredients to an aqueous environment, preferably the active ingredients  
30 being detergent active ingredients and the aqueous environment being the wash water. The elastic article can be such that delayed release of the active ingredient to the aqueous

environment can be achieved. The invention also relates to the use of an elastic article according to the invention to incorporate enzymes in compositions, preferably detergent compositions.

5 Detailed Description

Elastic article and matrix thereof

The elastic article of the invention comprises a matrix comprising, and formed from, a polymeric material and a plasticiser and optionally other materials. The matrix may comprise the active ingredient, or part thereof, or the active ingredient may be present  
10 outside the matrix, for example enclosed by the matrix ( the matrix coating or encapsulating the active ingredient). Thus, the polymer material and the active ingredient may be intimately mixed or even homogeneously mixed, in which case a so-called monophase elastic article is obtained, which has uniform physical and chemical properties. However, it may be preferred that the active ingredient and the polymeric  
15 material are present in the matrix in a non-homogeneous form, forming a multiphase elastic article, whereby on a microstructure level one or more of the active ingredients is present in lower or higher amounts in one area of the matrix than in an other area of the component, and thus lower or higher than the average obtained by intimate mixing.

20 It may also be preferred that the active ingredient is present in the core or an inner shell or layer of the article, enclosed by the matrix. It may also be preferred that part of the matrix forms a core or inner shell or layer of the article, which is then enclosed by a layer of the active ingredient and then preferably by another layer of the matrix material.

25 The elastic article comprises preferably at least 1% by weight of the active ingredients, more preferably from 5% to 70%, more preferably at least 10% by weight of the matrix, more preferably from 15% or even 20% or even 25% to 50%.

The elastic article comprises preferably from 10% to 99% by weight of the matrix, more  
30 preferably at least 20% or even 30% to 99%, more preferably from 20% or 30% to 90% to 80% by weight.

The plasticiser may consist of water, provided that it is then present at a level of at least 3% by weight of the article (based on free-moisture level). Preferably, at least a plasticiser other than water is present, as described below in more detail.

Essential to the invention is that the matrix has a glass transition temperature  $T_g$ , as defined below, of less than  $50^{\circ}\text{C}$ , preferably less than  $40^{\circ}\text{C}$  preferably less than  $20^{\circ}\text{C}$  or even less than  $10^{\circ}\text{C}$  or even less than  $0^{\circ}\text{C}$ . Preferably the glass transition temperature is above  $-20^{\circ}\text{C}$  or even above  $-10^{\circ}\text{C}$ .

The  $T_g$  of the matrix when used herein, is the  $T_g$  of the polymeric matrix as present in the article, which thus may be a mixture of polymeric material and plasticiser alone, or a mixture of polymeric material, plasticiser and active ingredient, and in either case, optional additional ingredients may be present (such as stabilisers, densification aids, fillers, lubricants etc., as described herein).

The glass transition temperature as used herein is as defined text book 'Dynamic Mechanical Analysis' (page 53, figure 3.11c on page 57), being the temperature of a material (matrix) where the material (matrix) changes from glassy to rubbery, namely where chains gain enough mobility to slide by each other.

The  $T_g$  of the matrix of the article of the invention can be measured in the Perkin-Elmer DMA 7e equipment, following the directions in operations manual for this equipment, generating a curve as illustrated in the book Dynamic Mechanical Analysis - page 57, figure 3-11c. The  $T_g$  is the temperature or log Frequency as measured with this equipment, between the glass and 'leathery region', as defined in that text.

The matrix, and preferably the elastic article as a whole, has a specific elasticity and flexibility, because of its specific glass transition temperature. In particular, this means that the matrix and the article reversibly deform, absorbing the energy of impacts or of forces so that the article or matrix remains substantially its original bulk volume after the

physical force seizes to be applied on the component.

The elasticity can be defined by the elastic modulus of the matrix, or even the article, which again can be defined by the Young's modulus. This can be calculated from strain  
5 or stress mechanical tests as known in the art, for example by using Perkin-Elmer DMA 7e equipment following the manufacturer's experimental procedure over a specific % static strain range, namely in the range of 10-40% static strain. This represents a maximum strain as could be applicable during normal manufacturing or handling. Thus, the elastic modulus as defined herein is the maximum modulus as measured with this  
10 equipment in the range of 10% to 40% static strain. For example a piece of matrix (or article) of 1 cm<sup>3</sup> can be used in the testing with this equipment.

The matrix herein typically has an elastic modulus or Young's modulus of less than 4 GN.m<sup>-2</sup>, or typically less than 2 GN.m<sup>-2</sup>, even more preferentially less than 1 GN.m<sup>-2</sup>, but  
15 typically even less than 0.5 GN.m<sup>-2</sup>, or even less than 0.1 GN.m<sup>-2</sup>, or even less than 0.01 GN.m<sup>-2</sup>, as measured with the Perkin-Elmer DMA 7e equipment. In particular a matrix herein which contains gas bubbles, e.g. formed by processes involving the introduction of air in the matrix, has an elastic modulus below 0.1 GN.m<sup>-2</sup> or even 0.01 GN.m<sup>-2</sup> or even below 0.005 GN.m<sup>-2</sup> or even below 0.0001 GN.m<sup>-2</sup>.

20

Preferably the matrix is flexible, such that it has a relative yield strain greater than 2%, and preferably greater than 15% or even greater than 50%, as measured with the Perkin-Elmer DMA 7e equipment. (The yield strain is in this measurement the limit deformation of a piece of matrix at which the it deforms irreversible).

25

In particular this means that when a matrix sample having a cross section of a specific length, for example 1cm, is compressed with a static force applied along the axis of that cross section, the static force being variable but at least equivalent to twice atmospheric pressure, the change of this length after removal of the force is at least 90% to 110% of  
30 the original length. This can for example be measured by use of Perkin-Elmer DMA 7e equipment.

Similarly, the matrix is preferably flexible to such an extent that when a matrix sample having a cross section of a specific length, for example 1 cm, is stretched with a static force applied along the axis of that cross section, the static force being variable, but at least equivalent to twice atmospheric pressure, the change of this length after removal of the force is at least 90% to 110% of the original length. This can for example be measured by use of Perkin-Elmer DMA 7e equipment.

In particular, when using this equipment, the static forces applied along the axis of a cross section of a 1 cm<sup>3</sup> matrix sample are gradually increased until the deformation of the component, in the direction of the cross section, is 70%. Then, the force is removed and the final deformation of the matrix sample in the direction of the cross section is measured. Preferably, this length of the cross section after this experiment is preferably from 90% to 110% of the original length of the cross section, preferably from 95% to 105% or even from 98% to 100%.

The elastic modulus or Young's modulus is related to the relative density, namely

$$\frac{E^*}{E_s} \approx \left( \frac{\rho^*}{\rho_s} \right)^2,$$

where  $\rho^*$  is the relative density of the matrix or even the article, and  $\rho_s$  is the relative densities of the components of the matrix or article, as described herein, and  $E^*$  is the Young's modulus of the matrix or even the elastic article itself, and  $E_s$  that of the components of the matrix or even the article. This means that even a stiff polymeric material, with a high  $E_s$  can be made into an elastic, flexible matrix by adjusting the levels and/ or type of plasticiser and optionally by modifying the density (or for example by introducing gas during the making process to form elastic foam articles, as described below).

The elastic article of the invention is typically used to deliver actives to aqueous environment. Then, the elastic article, and preferably the matrix thereof, is unstable when brought into contact with water. This occurs such that the active ingredients or part



thereof, present in the article is delivered to the water. Preferably the article or part thereof denatures, disintegrates, preferably disperses or dissolves in water. It may be preferred that the active ingredient is delivered rapidly and that the elastic article is such that the polymeric material of the matrix of the article disperses or dissolves rapidly;

5 preferably at least 10% of the polymeric material, by weight, is dissolved or dispersed in 30 minutes after contacting the article with water, or more preferably at least 30% or even at least 50% or even at least 70% or even at least 90% (introduced in the water at a 1% by weight concentration). It may even be preferred that this happens within 20 minutes or even 10 minutes or even 5 minutes after contacting the elastic article with the water. The

10 dissolution or dispersion can be measured by the method described herein after for measuring the dissolution and dispersion of polymers.

Preferably the elastic article is such that the total volume of the article is changed, preferably reduced, with at least 10%, compared to the initial total volume, as for

15 example can be determined when 1 cm<sup>3</sup> of the article is added to 100 ml of demineralised water upon and stirred for 5 minutes at a speed of 200rpm, at a temperature of 25°C. Preferably the change, or preferably reduction, in total volume is at least 20% or even at least 40% or even at least 60% or even at least 90% or even about 100%, e.g. because it may be preferred that substantially the whole article is disintegrated, dispersed or

20 preferably dissolved into the water quickly.

This can be measured by use of any method known in the art, in particular herein with a method as follows (double immersion technique):

1 cm<sup>3</sup> of an elastic article is obtained and introduced in a 100 ml micro volumetric

25 measuring cylinder which is filled with 50 ml ± 0.1ml of an organic inert solvent. Acetone is for example used when found to be neither denaturing and/or not interacting with the polymeric material in the matrix of the elastic article herein, for example when this is PVA. Other neutral organic medium can be used according to the nature of the article under investigation; the inert solvent is such that the article is substantially not

30 dissolved, dispersed, disintegrated or denatured by the solvent.

The cylinder is air sealed and left to rest for 1 minute so that the solvent penetrates the whole elastic article. The change in volume is measured and taken as the original volume  $V_i$  of the foam specimen. The article is then removed from the solvent and left to dry in air so that the solvent evaporates.

5

The article is then placed in a 250 ml beaker containing 100 ml of demineralised water, maintained at 25°C, under stirring at 200 rpm with the help of a magnetic stirrer, for 5 minutes. The remaining of the article specimen, if any, is filtered off with a 60mm mesh copper filter and placed in an oven at a temperature and for a period such that residual  
10 water is removed. The dried remaining article is re-introduced in the measuring cylinder which volume of acetone had been re-adjusted to 50 ml.

The increase in total volume is monitored and taken as the final volume of the elastic article  $V_f$ . The decrease in total volume  $\Delta V$  of the elastic article specimen is then:

$$\% \Delta V = \frac{V_f}{V_i} * 100$$

15

The matrix of the elastic article, or possibly even the article as a whole, has preferably a relative density  $\rho^*$  of from 0.01 to 0.95, more preferably from 0.05 to 0.9 or even from 0.1 to 0.8 or even from 0.3 to 0.7. The relative density is the ratio of the density of the matrix or the article ( $\rho^*$ ), to the sum of the partial densities of all the bulk materials used  
20 to form the matrix, or the article ( $\rho_s$ ).

The matrix or even the article as a whole, is preferably in the form of a foam and preferably such that it forms an interconnected network of open and/ or closed cells, in particular a network of solid struts or plates which form the edges and faces of open and/  
25 or closed cells. The spacing inside the cells can contain part of the active ingredient and/ or a gas, such as air.

Preferably, the ratio of the closed cells to open cells in the matrix of the article, or the article as a whole is more than 1:1, preferably more than 3:2 or even more than 2:1 or  
30 even more than 3:1. This ratio can be determined by calculating the Total Volume of a

specimen of the matrix or article,  $V_T$ , (assuming a spherical shape), and then measuring with a Mercury Porosimetry Test method the Open Cell Volume ( $V_O$ ) and subtracting the Open Cell Volume from the Total Volume should deliver the Closed Cell Volume ( $V_C$ :  $V_T = V_O + V_C$ .)

5

The preferred foamed article or foamed matrix, as used herein, is typically air-stable or stable upon contact with air, which means herein that the bulk volume of the article or matrix thereof substantially remains the same when exposed to air. This means in particular that the article or matrix thereof retains preferably from 75% to 125% or even from 90% to 110% or even from 95% to 100% of its bulk volume when stored in an open beaker (9 cm diameter; without any protective barrier) in a incubator under controlled ambient conditions (humidity = RH 60%, temperature = 25°C) for 24 hours. Preferably the elastic article or the matrix thereof, retains from 75% to 125% or even from 90% to 110% or even from 95% to 100% of its bulk volume under the above storage conditions whereby the humidity is 80%.

15

The bulk volume change can be measured by any conventional method. In particular useful is a digital image recorder system containing a digital camera coupled to a personal computer itself equipped with calibrated image analyser software. A 1cm<sup>3</sup> specimen of the article or the matrix thereof is obtained and introduced in an open beaker having a diameter of 9 cm and stored for 24 hours at the above conditions. After 24 hours, the size in all three dimensions is measured with the image analysis recorder system. Each specimen measurement is repeated three times, and the average bulk volume change is calculated in %.

25

Preferably, the elastic article or matrix thereof is such that, when in the form of particles of a mean particle size of 2000 microns or less, these particles also retain from 75% to 125% or even from 90% to 110% or even from 95% to 100% of their bulk volume. This can for example be measured by placing 20 grams of such particles, or a weight comprising more than 500 particles, in a volumetric beaker having a diameter of 9 cm. The beaker is taped lightly on its base until the elastic particles re-arrange themselves in a

30

stable position with a horizontal top surface. The volume is measured. The open beaker with the elastic particles is then carefully placed in the incubator for 24 hours, set to the desired %RH and temperature. The bulk volume after the 24 hours is measured and the change of bulk volume is calculated in %.

5

#### Polymeric Material and Plasticiser

Any polymeric material can be used to form the matrix herein, provided it has itself a T<sub>g</sub> as defined above or more typically, it can be formed into a matrix of the T<sub>g</sub> as defined above by using a suitable amount of plasticiser.

10

Preferably, the polymer material comprises or consists of amorphous polymer(s).

The polymeric material may consist of a single type of homologous polymer or may be a mixture of polymers. Mixtures of polymers may in particular be beneficial to control the mechanical and/or dissolution properties of the elastic article, depending on the application thereof and the requirements thereof.

15

Preferred it that the polymeric material comprises a water-dispersible or more preferably a water-soluble polymer.

20

Preferred water-dispersable polymers herein have a dispersability of at least 50%, preferably at least 75% or even at least 95%, as measured by the method set out hereinafter using a glass-filter with a maximum pore size of 50 microns; more preferably the polymer herein is a water-soluble polymer which has a solubility of at least 50%, preferably at least 75% or even at least 95%, as measured by the method set out hereinafter using a glass-filter with a maximum pore size of 20 microns, namely:

25

Gravimetric method for determining water-solubility or water-dispersability of polymers: 50 grams  $\pm$  0.1 gram of polymer is added in a 400 ml beaker, whereof the weight has been determined, and 245ml  $\pm$  1ml of distilled water is added. This is stirred vigorously on magnetic stirrer set at 600 rpm, for 30 minutes. Then, the water-polymer mixture is

30

filtered through a folded qualitative sintered-glass filter with the pore sizes as defined above (max. 20 or 50 microns). The water is dried off from the collected filtrate by any conventional method, and the weight of the remaining polymer is determined (which is the dissolved or dispersed fraction). Then, the % solubility or dispersability can be  
5 calculated.

Preferred are polymers selected from polyvinyl alcohols and derivatives thereof, polyethylene glycols and derivatives thereof, polyvinyl pyrrolidone and derivatives thereof, cellulose ethers and derivatives thereof, and copolymers of these polymers with  
10 one another or with other monomers or oligomers. Most preferred are PVP (and derivatives thereof) and/ or PEG (and derivatives thereof) and most preferably PVA (and derivatives thereof) or mixtures of PVA with PEG and/ or PVP (or derivatives thereof). Most preferred may also be a polymeric material only comprising PVA. Preferably, such polymers have a level of hydrolysis of at least 50%, more preferably at  
15 least 70% or even from 85% to 95%.

The polymer can have any average molecular weight, preferably from about 1000 to 1,000,000, or even from 4000 to 250,000 or even from 10,000 to 200,000 or even from 20,000 to 75,000. Highly preferred may be polymeric material having a weight average  
20 molecular weight of from 30,000 to 70,000.

Cross-linking agents may be added to modify the properties of the matrix and the resulting article as appropriate. Borate may be useful in the matrix.

25 Depending on the required properties of the article, the polymer material can be adjusted. For example, to reduce the solubility, polymers may be included in the material, which have high molecular weights typically above 50,000 or even above 100,000, and vice versa. For example, to change the solubility, polymers of varying level of hydrolyses may be used. For example, to improve (reduce) the elastic modulus, the cross-linking of the  
30 polymers may be increased and/ or the molecular weight may be increased.

It may be preferred that the polymer used in the elastic article herein has a secondary function, for example a function in the composition wherein article is to be incorporated. Thus for example for cleaning products, it is useful when the polymer in the polymeric material is a dye transfer inhibiting polymer, dispersant etc.

5

Any plasticiser which is suitable to aid the formation of a matrix as defined herein can be used. Mixtures of plasticiser may also be used. Preferably, when water is used, an additional plasticiser is present.

- 10 Preferably, the plasticiser or at least one of the plasticisers, has a boiling point above 40°C, preferably above 60°C, or even above 95°C, or even above 120°C, or even above 150°C.

- Preferred plasticisers include glycerol or glycerine, glycol derivatives including ethylene  
15 glycol, digomeric polyethylene glycols such as diethylene glycol, triethylene glycol and tetraethylene glycol, polyethylene glycol with a weight average M.W. of below 1000, wax and carbowax, ethanolacetamide, ethanolformamide, triethanolamine or acetate thereof, and ethanolamine salts, sodium thiocyanates, ammonium thiocyanates, polyols  
20 such as 1,3-butanediol, sugars, sugar alcohols, ureas, dibutyl or dimethyl phthalate, oxa monoacids, oxa diacids, diglycolic acids and other linear carboxylic acids with at least one ether group distributed along the chain thereof, water or mixtures thereof.

- The plasticiser is preferably present at a level of at least 0.5% by weight of the article, preferably by weight of the matrix, provided that when water is the only plasticiser it is  
25 present at a level of at least 3% by weight of the article, or preferably by weight of the matrix.

- Preferably, the plasticiser is present at a level of 1% to 35% by weight of the article or matrix, more preferably 2% to 25% or even to 15% or even to 10% or even to 8% by  
30 weight of the article or by weight of the matrix. The exact level will depend on the polymeric material and plasticiser used, but should be such that the matrix of the article

has the desired Tg. For example, when urea is used, the level is preferably 1% to 10% by weight of the matrix, while when glycerine or ethylene glycol or other glycol derivatives are used, higher levels may be preferred, for example 2% to 15% by weight of the article or matrix.

5

The ratio of plasticiser to polymeric material in the matrix is preferably 1 to 100, more preferably 1 to 70 or 1 to 50, more preferably 1 to 30 or even 1 to 20, again depending on the type of plasticiser and polymeric material used. For example, when the polymeric material comprises PVA and the plasticiser comprises glycerine or glycerol derivatives and optionally water, the ratio is preferably around 1:15 to 1:8, a preferred ratio being around 10:1.

10

#### Active Ingredient

The active ingredient can be any material which is to be delivered to a liquid environment, or preferably an aqueous environment and preferably an ingredient which is active in an aqueous environment. For example, when used in cleaning compositions the article can contain any active cleaning ingredients. The articles may also comprise compositions, such as cleaning composition or personal care compositions.

15

In particular, it is beneficial to incorporate in the elastic article active ingredients which are moisture sensitive or react upon contact with moisture, or solid ingredients which have a limited impact robustness and tend to form dust during handling.

20

The active ingredient is typically a moisture sensitive ingredient, a temperature sensitive ingredient, an oxidizable ingredient, a volatile ingredient, or a combination thereof. The active ingredient may be biological viable material, hazardous or toxic material an agricultural ingredient such as an agrochemical, a pharmaceutical ingredient such as a medicine or drug, or a cleaning ingredient.

25

In particular preferred in elastic articles are active ingredients, such as enzymes, perfumes, bleaches, bleach activators, fabric softeners, fabric conditioners, surfactants,

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such as liquid nonionic surfactant, conditioners, antibacterial agents, effervescence sources, brighteners, photo-bleaches and mixtures thereof.

Another active ingredient is a perhydrate bleach, such as metal perborates, metal  
5 percarbonates, particularly the sodium salts. Also preferred active ingredients are organic peroxyacid bleach precursor or activator compound, preferred are alkyl percarboxylic precursor compounds of the imide type include the N-,N,N<sup>1</sup>N<sup>1</sup> tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms such as  
10 tetraacetyl ethylene diamine (TAED), sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose, but also amide substituted alkyl peroxyacid precursor compounds

15 Highly preferred active ingredient for use in the elastic article herein are one or more enzymes. Preferred enzymes include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139. Preferred  
20 commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Preferred amylases include, for example,  $\alpha$ -amylases  
25 obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl, Duramyl and BAN by Novo Industries A/S. Highly preferred amylase enzymes maybe those described in PCT/ US 9703635, and in WO95/26397 and  
30 WO96/23873. The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or



Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomonas fluorescens.

Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

- 5 Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

10

Processes for making the elastic article

The elastic article of the invention can be made by any process of making a polymer matrix of the defined Tg from a polymeric material and a plasticiser, and combining an active ingredient with such a matrix. Preferred processes involve chemically or  
15 physically introducing a gas in a mixture of the polymeric material and plasticiser and optionally the active ingredient.

A preferred process for making the article herein comprising the step of

- 20 a) obtaining a mixture of a polymeric material and a plasticiser, preferably water and an additional plasticiser;
- b) chemically or physically introducing gas in said mixture of polymeric material and water;
- c) prior to step b) and/or simultaneously with step b) and/ or subsequently to step b), addition of the active ingredient to the mixture of polymer material  
25 and water;
- d) shaping of articles of the resulting mixture of step c);
- whereby one or more of steps a) to d) are followed or accompanied by removal of part of the water, if present.

- 30 Step c) preferably comprises the step of obtaining a body comprising the active ingredient or part thereof and enclosing said body with the mixture of step b).

In step a) the mixture is preferably an aqueous mixture or slurry and after or in step b), c) and/ or d), part of the water is removed such that the resulting article comprises 3% by weight of free-moisture, or more.

5

Preferably, the article comprises open and/ or closed cells and the process comprising the steps of

- a) formation of a mixture of the polymeric material, the active material, a plasticiser and a liquid, whereby the liquid and the plasticiser may be the same compound;
  - b) shaping of bodies from the mixture of claim b) and
  - b) evaporation of the liquid or part thereof to form spacings in the mixture which form the inner area of the cells of the article,
- whereby step c) is preferably conducted by freeze drying or by heating the bodies, thereby causing the liquid or part thereof to evaporate.

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Step b) may also be conducted by submitting the mixture of a) to pressure, preferably under mixing and/ or increasing the temperature, and subsequently removing the pressure or part thereof, thereby causing the liquid to evaporate. For example, an extrusion process can be used. Hereby it is preferred that the mixture of the polymeric material, plasticiser, preferably including water, and optionally the active ingredient, is introduced in an extruder, wherein the mixture is further mixed and heated, due to the mixing or due to applying heat, preferably such that the mixture therein forms a melt, and then dropping the pressure at the exit point where the extruded mixture (which can be formed into the desired form, for example granules) exits the extruder, whereby the liquid or part thereof evaporates, or preferably the water evaporates as steam from the extruded mixture. This results in formation of cells with spacings, as described above, which then may contain a gas, preferably air, and optionally the active ingredient. These spacings form the internal area of the cells of the matrix of the elastic article of the invention.

20  
25  
30

Step b) in the process may also be conducted by heating the mixture to cause the liquid or part thereof to evaporate, resulting in the formation of spacings, as above. This can preferably be done by feeding the mixture into a spray drying tower, preferably such that the mixture is fed through spray nozzles which form droplets of the mixture, and spray drying the droplets at conventional, resulting in granules of the elastic article.

The physical and/ or chemical introduction of gas or foaming, as mentioned above can be done by any known method, preferred are

- physical foaming by gas injection (dry or aqueous route) optionally under mixing, high shear stirring (dry or aqueous route), gas dissolution and relaxation including critical gas diffusion (dry or aqueous route);
- chemical foaming by in-situ gas formation (via chemical reaction of one or more ingredients, including formation of CO<sub>2</sub> by an effervescence system),
- steam blowing, UV light radiation curing.

These foaming steps are preferably followed by a drying step or an additional drying step to remove excess liquid or part thereof, such as water. In particular, the drying step is at least done after the polymer matrix is formed, and optionally after the active ingredient is added, preferably as final step in the process. The drying step is done preferably such that the final elastic article is of about the same volume after the drying step as before the drying step. Thereto, the drying step is preferably done by freeze-drying, whereby the solvent, e.g. water, is removed under vacuum and reduced temperatures. Also useful can be slow fluid bed drying or oven drying at modestly increased temperatures, such as 40-80°C, or even 40-60°C .

Preferred processes involve at least the step of formation of a mixture of polymeric material and a liquid, preferably a solution of polymeric material and a solvent, preferably comprising water, and adding a plasticiser (or as the case may be, additional plasticiser) to this. If the presence of the active ingredient in the matrix is required, this is also added to the mixture of polymeric material solvent and plasticiser. Alternatively, or in addition,

it may be preferred that the matrix is formed around the active material, preferably a core of the active material and carrier material.

This is then further processed for example into bodies of the shape of the final article, for example particles or beads, and typically dried to obtain the articles. Preferably, a gas is added prior to the shaping step. Shaping steps include granulation steps such as atomisation or spray-drying, extrusion, micro pastillation. Freeze drying is a preferred process to dry the bodies to form the articles.

The following are preferred processes resulting in low dust or even nil dust particles, as measured with the stressed Heubach test described below, having a matrix with a Tg of below 10°C and an elastic modulus of below 0.5GNm<sup>-2</sup>, as indicated in more detail in the following specific examples.

A first preferred process is as follows:

The required amount of a solution of the polymer material (or a mixture of polymer and a liquid) is obtained, and for example (introduced) in a mix tank. Then the required amount of (a solution of) the active material, for example an enzyme solution is added and the required amount of plasticiser is added, and optionally other additional ingredients, such as stabilisers, fillers, densification agents etc. This is agitated to become a homogeneous mixture. Preferably, a gas such as air can be introduced into the solution, by any of the methods above, preferably physically, by high sheer mixing.

Then, particles are formed from this mixture by atomisation, preferably using a Positive Displacement pump to transfer the mixture solution to a spray nozzle (s), preferably using either single or multi-fluid nozzles to create liquid droplets.

The liquid droplets are then frozen, preferably by passing through a refrigeration media (can include liquid nitrogen, freon, refrigeration oils). Then, the frozen particles are transferred to a vacuum chamber, preferably having a temperature (as measured on the surface of the particles) below 0°C.

The frozen particles are preferably collected from the spray column and transferred

without raising the temperature. The temperature of the walls and contact trays of the freeze dryer are preferably maintained below 0°C to keep the particles frozen.

A vacuum is applied, and the frozen ice crystals will sublime a gas form, resulting in cells in the particle. The total drying degree can be controlled with the level of vacuum,

5 and contact temperature of the chamber walls and trays.

After the particles have been dried to the desired moisture content, they will be free flowing. Then preferably, the particles can be classified via a variety of screens and or process equipment.

10 The optional step above, of introducing gas (bubbles) into the polymeric solution mixture has been found to give a much better impact resistance to the particle, reflected by its electric modules. The introduction of gas bubbles can be accomplished in a variety of ways.

15 In the atomisation step, the atomizing nozzle should preferably be located in a spray column with sufficient height to accomplish droplet freezing while gravity falling. The nozzle type can be of various designs - single fluid pressure nozzle, spinning insert, sonic, or multi-fluid nozzle. The important aspect is to disrupt the liquid stream to form discrete liquid droplets. As these droplets fall with gravity, they need to be cooled to  
20 freezing. The freezing media is preferably non-aqueous gas or liquid which can provide rapid freezing of the liquid droplets. The actual temperatures for cooling these droplets to form particles, is preferably below 0°C and preferably below -20°C.

It may also be preferred that the above process is modified as follows:

25 a gas, preferably CO<sub>2</sub> gas, is introduced in the mixture and the mixture is introduced in a spray drying tower, as above, thereby forming spray-dried foamed particles, which can be classified if necessary. Preferably the inlet temperature in the tower is about 130°C and the outlet temperature about 75°C and the spray rate is 12.5g/min. For example a Niro Mobil Minor with two fluid nozzles can be used hereby. The resulting particle may be  
30 already of the required form, or may be submitted to further freeze drying under vacuum.

Another preferred process is as follows:

The required amount of a solution of the polymer material is obtained (or alternatively, a powdered polymer can be used provided a liquid is added) and for example introduced in  
5 a mix tank. Then the required amount of plasticiser is added, and optionally other additional ingredients, such as stabilisers, fillers, densification agents etc. This is agitated to become a homogeneous mixture. Preferably, a gas such as air can be introduced into the solution, by any of the methods above, preferably physically, by high shear mixing.

10 Also, particles comprising the active ingredient and optionally other ingredients, such as fillers or carriers are prepared, for example by fluid bed coating, by charging first 'cores' (typically when the actives are enzymes, these core particles are sugar or starch particles), to a fluid bed and spraying the active material or a solution of the active  
15 material onto these cores and then drying any solvent such as water from the active solution off with warm fluidizing air.

Then, the polymeric mixture above is introduced onto these active/cores, for example via a positive displacement pump leading to an atomizing nozzle inside the fluid bed as  
20 described above. More than one nozzle can be used and it may be preferred that different ingredients are added to the core via different nozzles.

The fluidizing air needs is preferably below 0°C, preferably around -20°C. Then, the fluidizing air freezes the polymeric mixture/solution onto the outside of the active-core.  
25 This is a critical parameter to control and typically the air temperature must be below 0°C in order to quickly freeze the polymeric mixture/solution onto the core particles.

Then preferably, the frozen particles thus obtained are transferred to a vacuum chamber, as above, and also classification may take place.

30 This technology results in particle of the invention comprising a matrix around the active

ingredient.

The optional step above, of introducing gas (bubbles) into the polymeric solution mixture has been found to give a much better impact resistance to the particle, reflected by its Young's Modulus.

5

Another preferred process is as follows:

The required amount of a solution of the polymer material (or solid polymer and a suitable amount of liquid) is obtained, and for example introduced in a mix tank. Then the required amount of (a solution of) the active material, for example an enzyme solution  
10 is added (into the mix tank) and the required amount of plasticiser is added, and optionally other additional ingredients, such as stabilisers, fillers, densification agents. This is agitated to become a homogeneous mixture. Preferably, a gas such as air can be introduced into the solution, by any of the methods above, preferably physically, by high sheer mixing.

15

Then, the polymeric solution is pumped from the mix tank into an extruder or into a cavity with a die plate at the end. Before entering the extruder or cavity, gas can be injected into the mixture and for example be dispersed via a mechanical shear mixer or a static mixer.

20 As the extrudate exits the die plate, the change in pressure creates a slight puffing or swelling in the extrudate. The extrudate is then cut to the correct length with either a die face cutter or with some other device (eg. heated wire, rotating plug cutter, etc.). The extrudates can optionally go through additional rounding steps to become more spherical. Process equipment that can accomplish this function include (rotating pans,  
25 agglomeration pans, marumirizers, tumbling drums, mixing drums, etc.) .

For example, a paste is prepared by mixing 75g PVOH, 15g Citric acid, 2g PEO and 22.5g glycerol in a Braun mixer, high sheer, namely set at full speed for 40seconds: then 80g H<sub>2</sub>O and 80g enzyme was added and mixed at high sheer, namely set at full speed  
30 until a smooth foam had formed, approximately within 2mins. The foam was extruded from a 10ml syringe onto a plastic sheet. This was left for 24 hours to dry. Once dry the

foam strips were cut into approximately 1 - 2mm sections to form particles of the formula (dry) 63.2 polyvinyl alcohol, 19% glycerol, 12.7% citric acid, 1.6% PEO, 4% water, 3.2% enzyme.

- 5 The resulting particles had an elastic modulus of  $0.00016 \text{ GN.m}^{-2}$ .

The resulting particles give 0% dusting when tested in a stressed Heubach test, which indicated a very good impact robustness. (The stressed Heubach test is performed as known in the art, using equipment as supplied by Heubach Engineering GmbH,

- 10 Germany, with the stressed modification of the rotation speed of the impeller being  $75 \pm 1$  rpm and the balls being of Tungsten carbide and 82 grams each.).



Preferred moulding / pastillisation process:

A highly preferred process involves shaping particles of mixtures as described above by use of a mould; whereby mixtures as described herein are introduced in a mould and subsequently dried (freeze dried). Also preferred is such a process which uses pastille making equipment, whereby mixtures as described above, preferably comprising also introduced gas, are forced through a rotating perforated drum onto a moving conveyor belt, shaping into pastilles (droplets or particles). When dry or hardened, the thus formed particles or beads are removed from the conveyor belt by a scraper.

10 Preferably, the first step is to make a mixture of polymeric material and plasticiser, a liquid component, and optionally the active ingredient. Preferably, gas is introduced into this mixture as described herein. This must preferably be free from large undissolved particles which may block up the perforations in the drum. The mixture is preferably in the temperature range 0-50°C. The mixture is pumped into a manifold that enters the  
15 rotating perforated drum and is parallel to the longitudinal axis of the drum. The mixture is pumped into the inner of the drum and, as the drum rotates, is brought into contact with an internal scraper bladed lying in contact and along the length of the inner surface of the perforated drum, parallel to the feed manifold.

The distance of the outside surface of the perforated drum is within the height of the  
20 desired particle height (which is less than the diameter of the perforations) but not touching a moving conveyor belt or a rotating smooth surfaced drum at the point where the internal scraper is in contact with the inner surface of the perforated drum, the tangential speed of the perforated drum matched by the speed of the conveyor belt or the tangential speed of the smooth surfaced drum. As the mixture is forced through the  
25 perforations, which are typically in the size range 300 - 2000µm (but may be smaller or larger), it is deposited onto the surface below. The rotation of the perforated drum shears the feed material away from the material on the smooth surface thus leaving a droplet, or pastille, which will form the required particle. These pastilles can be set by either chilling or by evaporation of some or all of the solvent fluid. If chilling is required the  
30 temperature of the conveyor belt or smooth surfaced drum may be in the range ambient to -20°C. If evaporation of a solvent is required, then this can be achieved by heat

conduction from the conveyor belt which may be in the range ambient to 70°C, by drying air (which may be heated up to 200°C to reduce drying time) passing over the surface of the pastilles, or both.

Then, the resulting particles are removed from the drum or conveyor belt by a scraper.

- 5 This removal process may be improved by the use of a suitable lubricant (release agent) on the drum, such as silicone oil. This lubricant or release agent may show an added benefit to the particle by reducing adhesive properties between the polymeric mixture and the belt/drum and thus increasing the pastille height, if this is a desirable feature.

- 10 An example of this process is as follows:

- 4700g of a 33%w/w solution of polyvinyl alcohol (weight average M.W being from 30,000 to 70,000) is mixed with 159.3g of glycerol and 109.8g of citric acid in a high shear mixer until a smooth foam is formed. This mixture is transferred into a feed tank, and using a gear pump, it is pumped into micropastillisation equipment, for example as  
15 supplied by Sandvik Process Systems, Totowa New York, using a perforated drum with perforations of 1mm diameter, spaced 2.5mm apart. The apparatus deposits pastilles onto a smooth surfaced drum coated with a film of silicone oil and heated to ~30°C. When one quarter of the drum is covered by pastilles, the drum is stopped from rotating. The pastilles are dried using a hot air heater until the surfaces of the pastilles are dry to the  
20 touch. The resulting particles are then scraped off and collected.

The resulting particles had a elastic modulus of 0.001GN.m<sup>-2</sup>.

- The resulting particles give 0% dusting when tested in a stressed Heubach test, which  
25 indicated a very good impact robustness. (The stressed Heubach test is performed as known in the art, using equipment as supplied by Heubach Engineering GmbH, Germany, with the stressed modification of the rotation speed of the impeller being 75 ± 1 rpm and the balls being of Tungsten carbide, 82 grams each.)

Another example of making foamed articles of the invention, in the form of tablets, beads or particles, is as follows:

Apparatus: Microbalance, graduated 100ml flask, Kenwood "Chef" food processor with provided whisk and mixing bowl, glass or plastic moulds, spatula.

- 5    Chemicals: Poly (vinyl alcohol) (Aldrich chemicals, molecular weight  $M_w = 30-70k$ ), Glycerol (99 %, Aldrich chemicals), Citric Acid (Aldrich, Citric Acid, USP Anhydrous), distilled water, dry ice (or solid phase  $CO_2$ ), thermally insulated box.

Procedure

1. Weigh  $50 \pm 0.2$  grams of PVA,  $30 \pm 0.2$  grams of glycerol,  $20 \pm 0.2$  grams of citric acid.
- 10    2. Mix the PVA, glycerol and Citric acid using the mixer set a low speed (mark 2; low shear).
3. Add  $50 \pm 1$  ml of water gradually to the dry mix maintaining the mechanical mix for 2 minutes. A smooth gel should be obtained.
4. Increase the mix speed high sheer to the maximum setting (mark 8). Add 10-20 ml of
- 15    water until a PVA foam is forming. Maintain high shear mixing for 3 minutes.
5. The active ingredients, for example from 2-10 gram of enzyme, are progressively added to the foam under a maintained mechanical mixing so that a uniform active foam is obtained.
6. Stop mixing. Spread the PVA foam in moulds avoiding any collapsing of the structure.
- 20    7. Place the filled moulds in a thermally insulated box 1/3 filled with dry ice. Leave to freeze for 5 hours.
8. Quickly place frozen samples in a vacuum freeze-dryer (Edward XX) for 24 hours.
9. Remove dried sample from moulds.
- 25    Any active ingredient can be added in step 5, at any level, normally up to about 50 grams, for example fabric softeners, bleaching species, nonionic surfactants.

This was also repeated by using for example 40wt% polycarboxylic acid polymer, 30wt% diethyleneglycol, 15wt% amine oxide and as active ingredient 15wt% enzyme, softening

30    clay etc.; and repeated by using 40wt% polycarboxylic acid polymer, 30wt%

polyethylene glycol, 15wt% amine oxide and acid LAS (1:1) and as active ingredient 15wt% enzyme, softening clay etc.

Another example of making foamed articles of the invention, in the form of tablets, beads or particles, is as follows:

Apparatus: as described in the above example

Chemicals: Poly (vinyl alcohol) (Aldrich chemicals, molecular weight Mw= 30-70k), Glycerol (99 %, Aldrich chemicals), Citric Acid (Aldrich, Citric Acid, USP Anhydrous), Sodium carbonate (Aldrich, Anhydrous), Dodecyl Sulphate surfactant (Aldrich), distilled water, Petri dish (diameter 90 mm), Oven (set at 45 °C  $\pm$ 2°C)

Process:

1. Weigh 50  $\pm$ 0.2 grams of PVA, 30  $\pm$ 0.2 grams of glycerol, 20  $\pm$ 0.2 grams of citric acid, 20  $\pm$ 0.2 grams of sodium carbonate, and 2  $\pm$ 0.2 grams of dodecyl sulphate.
2. Mix the PVA, glycerol, citric acid and dodecyl sulphate using the mixer set a low speed (mark 2).
3. Add 50  $\pm$  1ml of water gradually to the dry mix maintaining the mechanical mix for 2 minutes. A smooth gel should be obtained.
4. Add the active ingredient, for example 5 gram enzyme, and sodium carbonate and mix vigorously for 30 second until a fully expanded foam is obtained
5. Spread the foam in petri dish in a uniform 1cm thick layer
6. Place petri dish in 40 °C oven for 24 hours.
7. Remove the dried foam film from mould.

Any active ingredient can be added in step 4, at any level, normally up to about 50 grams, for example fabric softeners, bleaching species, nonionic surfactants.

This was repeated by using 55wt% polycarboxylic acid polymer, 20wt% anhydrous sodium carbonate and 25wt% enzyme, softening clay etc.; and repeated by using 45wt% polycarboxylic acid polymer, 15wt% polyethylene glycol, 20wt% anhydrous sodium carbonate and 20wt% enzyme, softening clay etc.

Other preferred modifications

In the above processes, other polymer material mixtures of for example PVA and PVP or PEG were also used, and other plasticisers were used. Also, instead of the enzymes, other actives such as bleach or bleach activators or perfumes were used.

5

Preferred modification was also in any of the above processes that the gas introduced is carbon dioxide, CO<sub>2</sub>. This was done by introducing actual CO<sub>2</sub> gas into the polymer material/ plasticiser but this could equally be done by ingredients (such as effervescence sources) which chemically form CO<sub>2</sub> in the mixture.

10

Form of elastic article

The elastic article can be made into any form, by any conventional shaping method, some methods being described in detail above. Preferred may be that the elastic article is in the form of a particles, including pastilles and beads or in the form of tablets. The particles  
15 can be made by any granulation method, for example by granulation techniques such as atomisation, use of moulds or pastillisation equipment, grinding larger shapes of the elastic article, spray-drying, extrusion, as also described above.

Preferred elastic particles herein have a mean particle size of from 10 to 5000 microns,  
20 more preferably from 50 to 4000 microns or even to 2000 microns, even more preferably from 100 to 1500 microns or even from 200 or even 300 microns to 1000 microns.

The article herein may have a layered structure, having for example, a core of the active ingredient, enclosed by a layer of matrix, optionally coated or for example, a core of (part  
25 of) the matrix, enclosed with a layer of the active and then coated, for example with more of the matrix. The elastic article may also be in the form of a sheet, which can be obtained by any method, preferably by forming the sheet in a mould, as described above. When the elastic article is in the form of a sheet, the sheet can have any dimension and can be subsequently reduced in size as required. It may be preferred that the sheet has  
30 mean thickness of from 0.01 to 400 microns, more preferably from 0.05 to 200 microns, or even more preferably from 0.1 to 100 microns, or even 0.1 to 50 microns.

Additional Ingredients

The elastic article of the invention may preferably contain additional ingredients, such as process aids, stabilisers, lubricant, dispensing aids, pH regulators, solubilisers, including  
5 hydrotropes and disintegrating aids, densification aids, dyes, whitening agents, fillers, antioxidants and scavengers, perfumes.

Preferred additional agents are in particular effervescence sources, in particular based on organic carboxylic acids and carbonate sources. Preferred may be the use of citric acid,  
10 malic acid, maleic acid, fumaric acid or mixtures thereof, and for example salts (sodium) of percarbonate, carbonate and/ or bicarbonate. These may for example be comprised in the matrix. Preferred may be that the acid is present in the matrix and the carbonate in a different layer or core, or vise versa. It has been found that in particular the presence of an acidic material improves the dissolution and/or dispersion of the elastic article of the  
15 invention upon contact with water, and can also reduce or prevent interactions, leading to for example precipitation, of the polymeric material in the elastic article with cationic species present in the aqueous medium.

Phosphonate-based such as Chelating agents may also be preferred additional  
20 ingredients.

Preferred may also be to incorporate (in the polymer material) disintegrating polymers or water-swelleable polymers, which aid dissolution of the article. Thus, these may form part of the polymeric matrix herein. Examples of such aids are described in EP851025-A  
25 and EP466484-A.

Perfumes are also preferred ingredients of the article herein. Surfactants may also be added to the article, including certain nonionic surfactants which may also give a lubrication affect.

30

It may be preferred that inorganic salts or silicates are present, including zeolites and/ or phosphates.

Preferred additional ingredients are also ammonium compounds such as ammonium sulfate, ammonium citrate, and also granular urea, guanidine hydrochloride, guanidine carbonate, guanidine sulfonate, granular thiourea dioxide,

Colouring agent such as iron oxides and hydroxydes, azo-dyes, natural dyes, are also preferred, preferably present at levels of 0.001% and 10% or even 0.01 to 5% or even 0.05 to 1% by weight of the article.

Highly preferred additional ingredients include urea and/ or inorganic salts. Highly preferred may also be cross-linking agents, changing the crosslinking degree of the polymer material in the matrix. Borate may be useful.

Highly preferred may be that the article is coated with a coating agent, as known in the art, by any coating process. Preferred may be coating agents containing organic acids or salts, inorganic salts, additional polymers, having Tg of higher than 60°C, typically higher than 70°C.

Highly preferred is that the elastic article comprises (as pH-controller or dissolution aid) an acid such as citric acid, acetic acid, acetic acid glacial, fumaric acid, hydrochloric acid, malic acid, maleic acid, tartaric acid, nitric acid, phosphoric acid, sulfuric acid, pelargonic acid, lauric acid. Buffering agent which also boric acid, sodium acetate, sodium citrate, acetic acid, potassium phosphates and the likes.

The component of the invention preferably comprises additional ingredients which can improve the dissolution properties of the article herein.

Preferred additional ingredient which improve the dissolution of the article herein preferably comprise; a sulfonated compound such as C<sub>1</sub>-C<sub>4</sub> alk(en)yl sulfonates, C<sub>1</sub>-C<sub>4</sub>

aryl sulfonates, di iso butyl benzene sulphonate, toluene sulfonate, cumene sulfonate, xylene sulfonate, salts thereof such as sodium salts thereof, derivatives thereof, or combinations thereof, preferably di iso butyl benzene sulphonate, sodium toluene sulfonate, sodium cumene sulfonate, sodium xylene sulfonate, and combinations thereof;  
5 and/or a C<sub>1</sub>-C<sub>4</sub> alcohol such as methanol, ethanol, propanol such as iso-propanol, and derivatives thereof, and combinations thereof, preferably ethanol and/or iso-propanol; and/or a C<sub>4</sub>-C<sub>10</sub> diol such as hexanediol and/or cyclohexanediol, preferably 1,6-hexanediol and/or 1,4-cyclohexanedimethanol; and/or ingredients which are capable of acting as whicking agents, such as cellulosic based ingredients, especially modified  
10 cellulose; and/or swelling agents such as clays, preferred clays are smectite clays, especially dioctahedral or trioctahedral smectite clays, highly preferred clays are montmorillonite clay and hectorite clay, or other clays found in bentonite clay formations; and/or an effervescence system, a preferred effervescence system comprises an acid source capable of reacting with an alkali source in the presence of water to  
15 produce a gas.

The component of the invention preferably comprises additional ingredients which can improve the stability of the active ingredient of the article herein.

20 These additional ingredients are typically capable of stabilising the active ingredient of the component herein, this is especially preferred when the active ingredient(s) comprise an oxidative or moisture sensitive active ingredient, such as one or more enzymes. These additional ingredients may also stabilise the matrix of the component herein, and thus indirectly stabilise the active ingredient. These stabilising ingredients are defined herein  
25 as "stabilising agents".

The stabilising agent is preferably a compound which stabilises the active ingredient, or matrix, from oxidative and/or moisture degradation during storage. The stabilising agent may be, or comprise, a foam matrix stabiliser. The stabilising agent may be, or comprise,  
30 an active ingredient stabiliser, especially an enzyme stabiliser. Stabilising agents which are capable of stabilising the active ingredient indirectly by keeping the foam matrix of



the article stable, herein referred to as "foam stabiliser".

Foam stabilisers preferably comprise a surfactant such as a fatty alcohol, fatty acid, alkanolamide, amine oxide, or derivatives thereof, or combinations thereof. The foam  
5 stabiliser may comprise betaine, sulfobetaine, phosphine oxide, alkyl sulfoxide, derivatives thereof, or combinations thereof.

Other preferred foam stabilisers comprises one or more anions or cations such as mono-, di-, tri- valent, or other multivalent metal ions, preferred are salts of sodium, calcium,  
10 magnesium, potassium, aluminium, zinc, copper, nickel, cobalt, iron, manganese and silver, preferably having an anionic counterion which is a sulphate, carbonate, oxide, chloride, bromide, iodide, phosphate, borate, acetate, citrate, and nitrate, and combinations thereof.

15 The foam stabiliser may comprise finely divided particles, preferably finely divided particles having an average particle size of less than 10 micrometers, more preferably less than 1 micrometer, even more preferably less than 0.5 micrometers, or less than 0.1 micrometers. Preferred finely divided particles are aluminosilicates such as zeolite, silica, or electrolytes described hereinbefore being in the form of finely divided particles.

20

The foam stabiliser may comprise agar-agar, sodium alginate, sodium dodecyl sulfate, polyethylene oxide, guar gum, polyacrylate, or derivatives thereof, or combinations thereof.

25 The foam stabiliser may be coating which is separate to the matrix of the article herein. The foam stabiliser typically partially encloses, preferably completely encloses, the article herein or the active ingredient thereof.

The coating is typically contacted to, preferable in such a manner as to form a coat on, the  
30 active ingredient prior to said active ingredient being contacted to the polymeric material or the plasticiser of the matrix, and preferably being incorporated in the article herein.

The coating may typically be contacted to, preferable in such a manner as to form a coat on, the article herein subsequent to the polymeric material and the plasticiser forming the matrix, and preferably subsequent to the active ingredient contacting said matrix or being  
5 incorporated in the article herein.

Preferred coating comprises polymers, typically selected from polyvinyl alcohols and derivatives thereof, polyethylene glycols and derivatives thereof, polyvinyl pyrrolidone and derivatives thereof, cellulose ethers and derivatives thereof, and copolymers of these  
10 polymers with one another or with other monomers or oligomers. Most preferred are PVP (and derivatives thereof) and/ or PEG (and derivatives thereof) and most preferably PVA (and derivatives thereof) or mixtures of PVA with PEG and/ or PVP (or derivatives thereof). These polymers do not form the matrix of the article herein. Thus, these polymers are different to the polymeric materials of the foam matrix.

15 A preferred coating comprises compounds such as glycerol or glycerine, glycol derivatives including ethylene glycol, digomeric polyethylene glycols such as diethylene glycol, triethylene glycol and tetraethylene glycol, polyethylene glycol with a weight average M.W. of below 1000, wax and carbowax, ethanolacetamide, ethanolformamide, triethanolamine or acetate thereof, and ethanolamine salts, sodium thiocyanates,  
20 ammonium thiocyanates, polyols such as 1,3-butanediol, sugars, sugar alcohols, ureas, dibutyl or dimethyl phthalate, oxa monoacids, oxa diacids, diglycolic acids and other linear carboxylic acids with at least one ether group distributed along the chain thereof, water or mixtures thereof. These compounds do not form the foam matrix of the article herein.  
25 Thus, these compounds are different to the plasticiser of the foam matrix.

Preferred stabilising agents that are capable of stabilising the active ingredient directly, especially if said active ingredient comprises one or more enzymes, are defined herein as “active stabilisers” or “enzyme stabilisers”. Typically active stabilisers interact directly  
30 with, and stabilise, the active ingredient.

Typical active stabilisers for use herein preferably comprise a surfactant. Suitable surfactants for use herein are those described hereinbefore as surfactants suitable for use as matrix stabilisers. In addition to these surfactants, other surfactants suitable for use herein may comprise surfactants such as sodium alky(en)yl sulfonates, sodium  
5 alcoxysulfonates, preferred alcoxysulfonates are those comprising from 10 to 18 carbon atoms in any conformation, preferably linear, and having an average ethoxylation degree of from 1 to 7, preferably from 2 to 5.

Other preferred active stabilisers comprise boric acid, formic acid, acetic acid, and salts  
10 thereof. These acid salts preferably comprise counterions such as calcium and/or sodium.

Preferred active stabilisers comprise cations such as calcium and or sodium. Preferably calcium chloride and/or sodium chloride.

15 Other preferred active stabilisers comprise small peptide chains averaging from 3 to 20, preferably from 3 to 10 amino acids, which interact with and stabilise the active ingredient, especially enzyme(s).

Other active stabilisers comprise small nucleic acid molecules, typically comprising from  
20 3 to 300, preferably from 10 to 100 nucleotides. Typically nucleic acid molecules are deoxyribonucleic acid and ribonucleic acid. The nucleic acid molecules may be in the form of a complex with other molecules such as proteins, or may form a complex with the active ingredient of the article herein, especially enzyme(s).

25 Active stabilisers suitable for use herein, especially when the article herein comprises a bleach, comprise anti-oxidants and/or reducing agents such as thiosulphate, methionine, urea, thiourea dioxide, guanidine hydrochloride, guanidine carbonate, guanidine sulfamate, monoethanolamine, diethanolamine, triethanolamine, amino acids such as glycine, sodium glutamate, proteins such as bovine serum albumin and casein, tert-  
30 butylhydroxytoluene, 4-4,-butylidenebis (6-tert-butyl-3-methyl-phenol), 2,2'-butylidenebis (6-tert-butyl-4-methylphenol), (monostyrenated cresol, distyrenated cresol,

monostyrenated phenol, distyrenated phenol, 1,1-bis (4-hydroxy-phenyl) cyclohexane, or derivatives thereof, or a combination thereof.

Other active stabilisers may comprise a reversible inhibitor of the active ingredient.

- 5 Without wishing to be bound by theory, it is believe that a reversible inhibitor of the active ingredient, especially if the active ingredient comprises one or more enzymes, may form a complex with, and improve the stability of, said active ingredient, and thus, stabilises the active ingredient during storage. When the active ingredient is released, typically into a liquid environment, the reversible inhibitor dissociates from the active  
10 ingredient and the active ingredient is then able to perform the desired action it is designed or intended to perform.

- Active stabilisers suitable for use herein may comprise sugars, Typical sugars for use herein include those selected from the group consisting of sucrose, glucose, fructose,  
15 raffinose, trehalose, lactose, maltose, derivatives thereof, and combinations thereof.

The active stabiliser may also comprise sugar alcohols such as sorbitol, mannitol, inositol, derivatives thereof, and combinations thereof.

- 20 It may be preferred that the active stabiliser is in the form of a coating or barrier which at least partially encloses the article herein or the active ingredient thereof, preferably completely encloses the article herein or the active ingredient thereof, especially an enzyme.

25 Compositions comprising the elastic article

The elastic article may be incorporated in any compositions which requires active ingredients to be protected against moisture during storage, against chemical reactions with other ingredients, migration or phase separation of ingredients, or protection against physical forces.

In particular, the elastic article is useful in cleaning compositions, fabric care compositions, personal care compositions, cosmetic compositions, pharmaceutical compositions. These compositions may are typically solid. They may comprise any additional ingredients, including additional amounts of the active ingredients or  
5 polymeric material described above.

Preferred are laundry and dish washing detergent compositions and fabric conditioners and other rinse aids. The cleaning compositions typically contain one or more components selected from surfactants, effervescence sources, bleach catalysts, chelating  
10 agents, bleach stabilisers, alkalinity systems, builders, phosphate-containing builders, organic polymeric compounds, enzymes, suds suppressors, lime soap, dispersants, soil suspension and anti-redeposition agents, soil releasing agents, perfumes, dyes, dyed speckles, brighteners, photobleaching agents and additional corrosion inhibitors.

15 For laundry detergent compositions and fabric care compositions it may be preferred that the article preferably comprise at least one or more softening agents, such as quaternary ammonium compounds and/ or softening clays, and preferably additional agent such as anti-wrinkling aids, perfumes, chelants, fabric integrity polymers.

20 In personal-care products it may be highly preferred to include cationic organic compounds, such as cationic surfactants. It can be preferred that the compositions comprise one or more other ingredient which can reduce dermatitis or compounds which can help the healing of the skin, metal-containing compounds, in particular zinc-containing compounds, vitamins and cortisone's, and also compounds to soften the skin  
25 such as vaseline, glycerin, triethyleneglycol, lanolin, paraffin and another group of polymers extensively employed by pharmaceutical and cosmetic manufactures, as also described herein.

The pharmaceutical compositions, cosmetic compositions and personal care  
30 compositions can be of any form and purpose. Preferred are pharmaceutical powders and tablets. The elastic article can also be incorporated in absorbing articles, for example to

release the actives of the elastic article to the skin whereto the absorbing articles is applied, when in contact with water, such as body fluids, for example diapers, wipes, catamenials, plaster, bandages.

WHAT IS CLAIMED IS:

1. An elastic article comprising
  - a) an active ingredient;
  - 5 b) a matrix formed from a polymeric material and a plasticiser, provided that when the plasticiser consists of water, the level is at least 3% by weight, whereby the article is capable of delivering the active to a liquid environment, and whereby the matrix has a glass transition temperature ( $T_g$ ) below  $50^{\circ}\text{C}$ , preferably below  $40^{\circ}\text{C}$ , and whereby the active ingredient or part thereof may be present in the
- 10 matrix.
2. An article as in claim 1 whereby the active ingredient is active in aqueous environment and the article is water-dispersable, water-disintegrating or water-soluble, preferably the matrix is water-soluble.
- 15 3. An article according to claim 1 or 2 whereby the matrix has a  $T_g$  between  $-20^{\circ}\text{C}$  and  $20^{\circ}\text{C}$ , preferably even between  $-10^{\circ}\text{C}$  and  $10^{\circ}\text{C}$ , and an elastic modulus of less than  $1 \text{ GN.m}^{-2}$ , preferably less than  $0.1 \text{ GN.m}^{-2}$ , or even less than  $0.01 \text{ GN.m}^{-2}$ .
- 20 4. An elastic article according to any of claims 1 to 3, which is in the form of a foam which is stable upon contact with air and unstable upon contact with water, said elastic foam article preferably having an elastic modulus of less than  $0.1 \text{ GN.m}^{-2}$  or even below  $0.01 \text{ GN.m}^{-2}$ .
- 25 5. An elastic article according to any preceding claim comprising from 30% to 90% by weight of the matrix and from 5% to 70% by weight of water and from 1% to 15% by weight of a plasticiser, preferably including at least 3% by weight of free moisture.
- 30

6. An article according to any of claims 1 to 5 obtainable by a process comprising the step of
- a) obtaining a mixture of a polymeric material and a plasticiser, preferably water and another plasticiser;
  - 5 b) chemically or physically introducing gas in said mixture of polymeric material and water;
  - c) prior to step b) and/or simultaneously with step b) and/ or subsequently to step b), addition of the active ingredient to the mixture of polymer material and water;
  - 10 d) shaping of articles of the resulting mixture of step c);
- whereby preferably one or more of steps a) to d) are followed or accompanied by removal of part of the water, if present.
7. An article according to claim 6, whereby step c) of the process as in claim 6
- 15 comprises the step of obtaining a body comprising the active ingredient or part thereof and enclosing said body with the mixture of step b).
8. An article as in claim 6 or 7 whereby in step a) the mixture is an aqueous mixture and after or in step b), c) and/ or d) of claim 6 part of the water is removed such
- 20 that the resulting article comprises at least 3% by weight of free-moisture.
9. An elastic article according to claim 4, whereby the foam article comprises cells, obtainable by a process comprising the steps of
- a) formation of a mixture of the polymeric material, the active material, plasticiser
  - 25 and a liquid, whereby the liquid and the plasticiser may be the same compound;
  - b) shaping of bodies from the mixture of claim b) and
  - b) evaporation of the liquid or part thereof to form spacings in the mixture which form the inner area of the cells of the article,
- whereby step c) is preferably conducted by freeze drying or by heating the bodies,
- 30 thereby causing the liquid or part thereof to evaporate.



10. An elastic article according to any preceding claim whereby the polymeric material comprises a water-soluble polymer, preferably a polyvinylalcohol.
- 5 11. An elastic article according to any preceding claim which has a relative density of 0.05 to 0.9, preferably 0.3 to 0.7.
12. An elastic article according to any preceding claim comprising closed and open cells, preferably the ratio of closed to open cells being at least 1:1.
- 10 13. An elastic article according to any preceding claim whereby the active ingredient is a cleaning product ingredient, fabric care ingredient, pharmaceutical ingredient or cosmetic ingredient, preferably selected from enzymes, perfumes, surfactants, brighteners, dyes, suds suppressers, bleaches, bleach activators, fabric softeners, fabric conditioners, antibacterial agents, effervescing systems and mixtures thereof. .
- 15 14. An elastic article according to claim 13 whereby the active ingredient comprising at least an enzyme.
- 20 15. An elastic article according to any preceding claim which is in the form of a granule, bead or tablet.
16. A according to claim 15 in the form of a particle or bead having a mean particle size of from 50 to 4000 microns, preferably from 100 to 1500 microns.
- 25 17. An elastic article according to any preceding claim, comprising a cleaning composition, fabric care composition cosmetic composition or pharmaceutical composition.

18. A cleaning composition, fabric care composition, cosmetic composition, personal care composition or pharmaceutical composition comprising the elastic article according to any of claims 1 to 16.
19. A process as in claim 6, 7 or 9.
- 5 20. A process as in claim 19 comprising the step of introducing gas in a mixture comprising at least the polymeric material, water, another plasticiser and optionally the active ingredient to form a foam and subsequently forming particles, beads or tablets from the foam, by use of a spraying process, extrusion process, moulding process or micropastillisation process, the process comprising at least one drying step.
- 10 21. Use of an elastic article according to any of claims 2 to 17 to deliver active ingredients to an aqueous environment, preferably the active ingredients being detergent active ingredients and the aqueous environment being the wash water.
- 15 22. Use of a elastic article according to any of claims 2 to 17 in cleaning compositions, fabric care compositions, personal care compositions, cosmetic compositions or pharmaceutical compositions, preferably to incorporate therein active ingredients selected from enzymes, perfumes, surfactants, brighteners, dyes, suds suppressers, bleaches, bleach activators, fabric softeners, fabric conditioners, antibacterial agents, effervescing systems, and mixtures thereof
- 20

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/27333

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08J9/30 C08J9/28 C09D5/00 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J C09D C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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International Application No

PCT/US 00/27333

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